

CRYSTAL FIELD EFFECTS AND SIDEROPHILE ELEMENT PARTITIONING: IMPLICATIONS FOR MARS HSE GEOCHEMISTRY. J.H. Jones¹, V. Malavergne², and C.R. Neal³. ¹KR, NASA/JSC, Houston, TX 77058 (john.h.jones@nasa.gov); ²Laboratoire des Géomatériaux, Université de Marne La Vallée, 77454 Marne la Vallée, France; ³Dept. Civil Engineering & Geological Sciences, 156 Fitzpatrick Hall, U. of Notre Dame, Notre Dame, IN 46556.

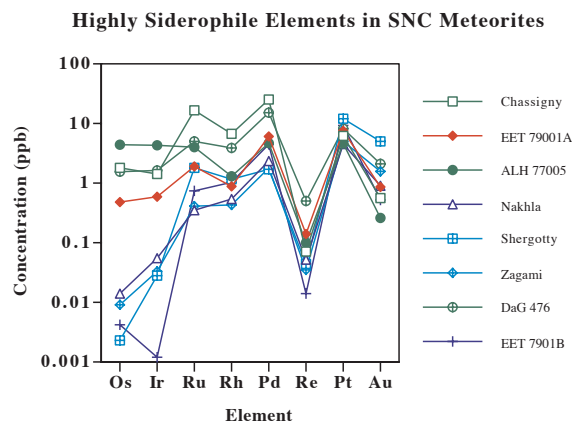
Introduction: Analyses of martian (SNC) meteorites indicate that Pt abundances do not vary much compared to other highly siderophile elements (HSE). Therefore, Jones et al. [1] inferred that $D(\text{Pt})$ during basalt petrogenesis was of order unity. This inference was at odds with previously published experiments that gave a $D_{\text{ol/liq}}$ for Pt of ~ 0.01 [2]. Because olivine is likely to be an important constituent of any reasonable martian mantle, the implication of these findings is that minor minerals must have $D(\text{Pt}) \gg 1$, which seemed improbable.

However, not only did the SNC evidence point to a $D_{\text{ol/liq}} \sim 1$, but so did plots of $D_{\text{ol/liq}}$ vs. ionic radius (Onuma diagram). The ionic radius of Pt^{2+} suggested that $D_{\text{ol/liq}}$ for Pt was of order unity, in agreement with the inferences from SNC meteorites.

New experiments have failed to detect measurable Pt in olivine, even at high oxygen fugacities [3]. Therefore, some other parameter, other than ionic charge and radius, must hold sway during olivine-liquid partitioning of Pt.

The SNC Evidence: Figure 1 shows HSE abundances in SNC meteorites. Some elements such as Os and Ir are highly fractionated. However, Pt is not fractionated much at all. Of course, this is a log scale and small ($\sim 2X$) variations can be obscured. In fact, we will argue below that there really is significant variation of Pt within the SNC suite.

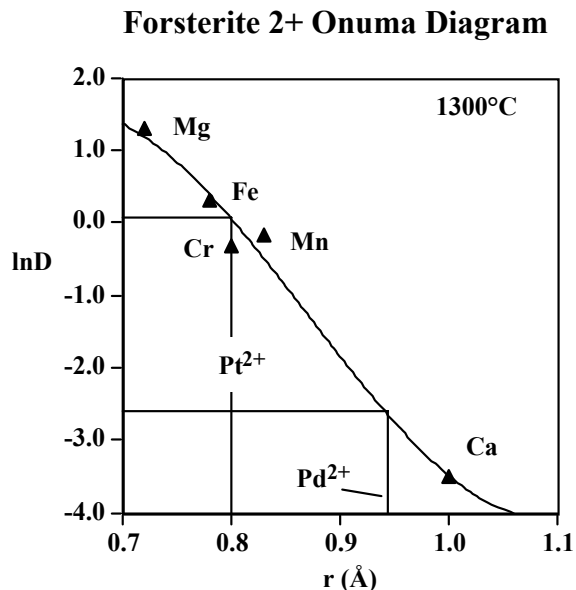
Figure 1



Onuma Diagram Evidence: Figure 2 shows the predicted $D(\text{Pt})$ for olivine/liquid based on the ionic

radius of Pt^{2+} . The valence of Pt in our experiments is inferred from the experiments of [4].

Figure 2



Based on Figure 2 we predicted that $D(\text{Pt})_{\text{ol/liq}}$ would be ~ 1 .

Experimental Partitioning Evidence: Our current experiments on a martian basalt composition (Eg), whose f_{O_2} 's range from air to QFM, produce olivines with no detectable Pt. There is Pt in the silicate liquid but none in the olivines. We believe our experiments have closely approached equilibrium, based on $K_D(\text{Fe}/\text{Mg})$ for olivine/liquid. Our value for $D(\text{Ru})_{\text{ol/liq}}$ is also in agreement with those of [2] and [5].

Interpretation: Thus, we have our dilemma. Martian basalts indicate that Pt abundance does not change much during SNC petrogenesis. Simple charge and ionic radius considerations support this view. However, Pt does not readily enter olivine in our experiments, and must have a $D_{\text{ol/liq}}$ that is very small [2,3].

We believe that the solution to this paradox is that Pt is strongly disinclined to enter octahedral M sites in olivine because of crystal field effects. Cotton and

Wilkinson [6] note that Pt^{2+} in octahedral coordination is almost unknown. More recently, Greenwood and Earnshaw [7] give examples of octahedral Pt^{2+} but note their rarity.

At first glance, this interpretation seems problematic. Pt^{2+} has the same electronic structure as Ni^{2+} , which enters olivine readily (e.g., Fig. 2). However, crystal field effects grow stronger as atomic number increases (within a periodic column). Presumably, this is because of the increasing size of the d orbitals being filled. In the case of Pt and Ni, it would be the size difference between 5d and 3d orbitals.

There appears to be periodicity in the magnitude of the crystal field effect. Figure 2 shows that $D(Pd)_{ol/liq}$ is predicted to be ~ 0.1 , but the actual measured value is ~ 0.01 [2,5]. So, going down the column, Ni is quite happy in octahedral sites. There is indication that Pd avoids octahedral sites $\sim 10X$ more than Onuma diagrams predict. And it appears that Pt avoids octahedral sites $\sim 100X$ more than predicted by Onuma diagrams. Therefore, we believe that the observed increasing distaste for octahedral coordination as one goes down the column Ni-Pd-Pt is consistent with known crystal field tendencies and with our observation that Figure 2 is inadequate to explain Pt and Pd partitioning into olivine.

Discussion: The above introduction appears to preclude olivine or low-Ca pyroxene as a significant reservoir for Pt in planetary mantles. Yet, the clustering of Pt analyses in Figure 1 remains to be explained. Exacerbating this problem is the observation that some SNC's, such as the nakhlites and chassignites, were produced by very small degrees of partial melting [8]. If $D(Pt)$ is also small, then small degrees of partial melting will promote Pt fractionation between melt and residue.

One possibility is that the Pt analyses are somehow compromised. We do not believe this to be the case. Interlaboratory comparisons of HSE's in SNC's are reasonably good [1].

Another possibility is that Pt (and other HSE's) reside in sulfides and its abundance is being buffered at a constant value. Again, we reject this interpretation. Jones et al. [1] showed that the overall HSE pattern in SNC's varies quite systematically with MgO content. This correlation with a highly lithophile element argues against sulfide buffering. In addition, it is obvious (Fig. 1) that the other HSE's are not buffered at all.

Another possibility, as yet untested, is that Pt has reasonably large (i.e., 1-10) partition coefficients into minor phases in the martian mantle. The obvious choices are garnet and Ca-rich pyroxene, because they

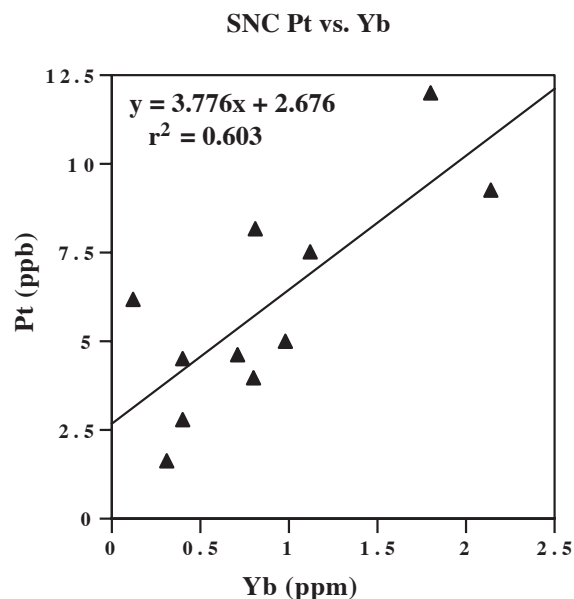
have M sites that are not octahedral. One $D(Pt)_{cpx/liq}$ from [5] is supportive of this hypothesis.

Another observation that must be explained is that Pt correlates reasonably well with Yb (Figure 3). Figure 3 is both liberating and constraining. It is liberating in that $D(Pt)$ need no longer be close to unity. Yb is a modestly incompatible element with a bulk D of ~ 0.1 - 0.3 . If Pt correlates with Yb, then $D(Pt)$ should be similar to $D(Yb)$. Figure 3 is also liberating in that significant variation ($\sim 5X$) in bulk Pt concentration is allowed.

Figure 3 is also constraining because (considering analytical and sampling issues) a factor of five variation is not that large. As discussed above, the combination of a small $D(Pt)$ and small degrees of partial melting invites large fractionations.

Earlier (for crystal field reasons) we suggested that garnet and Ca-rich pyroxene might make good hosts for Pt. In the absence of phosphate, these phases are also likely to dominate the geochemical behavior of Yb. Thus, the correlation of Pt and Yb reinforces our earlier suggestion.

Figure 3



References: [1] Jones J.H. et al. (1993) *Chem. Geol.* **196**, 21-41. [2] Brenan J.M. et al. (2003) *E.P.S.L.* **212**, 135-150. [3] Malavergne V. et al. (2006) *Lun. Plan. Sci. XXVII*, #1974. [4] Borisov A. and Palme H. (1997) *G.C.A.* **61**, 4349-4357. [5] Righter K. et al. (2004) *G.C.A.* **68**, 867-880. [6] Cotton and Wilkinson (1966) *Advanced Inorganic Chemistry*. [7] Greenwood N.N. and Earnshaw A. (1984) *Chemistry of the Elements*. pp. 1349-1354. [8] Longhi J. (1991) *Proc. Lunar Planet. Sci. Conf. 21st*, 695-709.